may then be depended upon except in those cases in which the amount of magnesium present is ten times as great as the calcium.

Conclusions.—In the determination of calcium in mixtures of calcium and magnesium carbonates no difficulty is experienced in obtaining a good separation of the calcium by a single precipitation if 0.6 g. of the sample is employed, if the solution contains 3.5 g. of ammonium chloride and is diluted to 300 cc. and heated to boiling before precipitation, if precipitation is effected by the addition of 1 g. of oxalic acid and neutralization, during an interval of five minutes, with a one per cent. solution of ammonium hydroxide, and if the precipitate is allowed to stand for an hour, provided the amount of magnesium present does not greatly exceed the amount of calcium. If the relative amount of magnesium present is still greater this method should be further modified by effecting precipitation in two stages, during the first of which only sufficient precipitant to combine with all the calcium present is added. If the amount of magnesium is ten times as great as the calcium it is difficult to obtain a perfect separation by a single precipitation.

Finally it may be noted that the coarsely crystalline character of the precipitate which is obtained when the calcium oxalate is separated from an acid solution is in itself a sufficient object to justify the exclusive use of this method of making the precipitation.

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A STUDY OF THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

I. THE COMPOSITION OF THE REAGENT AND OF THE REACTION PRODUCT.

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The use of phenolsulphonic acid for the detection and determination of nitrates was first proposed by Sprengel (1) in 1863, and attention was called to this suggestion by Kekulé (3, 6) in 1867, who incorporated the method in his *Lehrbuch*, but it was not until 1885 that the process was placed upon a practical basis by Grandval and Lajoux (2) and described by them in substantially the same form in which it is used today. Briefly this consists in pouring over the dry nitrate-containing material a few cubic centimeters of a mixture of phenol dissolved in concentrated sulphuric acid. After standing a few moments, water is added and the mixture made alkaline with ammonium hydroxide or sodium or potassium hydroxide. The yellow color resulting is then matched in a colorimeter with a similarly treated known amount of nitrate.

Grandval and Lajoux believed that their reagent contained a mono-sulphonic acid of phenol and that the yellow color obtained in the final reaction was due to the formation of an alkali salt of picric acid. Fox (27) published in the same year a few modifications of the Grandval and Lajoux method but held to the hypothesis of mono-phenol-sulphonic acid in the reagent and picric acid in the final product.

No protest against this theory was raised in spite of much work done upon the method until Hazen and Clark (33) demonstrated that the color of the final product could not be due to salts of picric acid since alkaline solutions of picric acid gave entirely different colors from those obtained by treating a small amount of nitrate with the reagent. These authors found, however, that the color could be exactly duplicated by alkaline mixtures of various mononitrophenols. From a study of such solutions they concluded that the reaction product was chiefly paranitrophenol.

In the meantime it had been shown that variable results were often obtained and that the reagent probably had a variable composition. This phase of the question was attacked by Gill (34) with the object of obtaining a reagent of definite composition and one which would not change on standing. Falling back upon Kekulé's (6, 15) work on the phenolsulphonic acids, Gill proposed heating a mixture of phenol and sulphuric acid on the water-bath, thus obtaining what was believed to be a disulphonic acid, probably the 1–2–4. This hypothesis is now known to be correct, although much of the work of Kekulé was wrong. Gill, however, followed Kekulé's theory that when the phenoldisulphonic acid was poured over a nitrate, picric acid resulted.

Montanari (39) adopted a process somewhat similar to that of Hazen and Clark for the investigation of the final yellow compound obtained in the method, and concluded that no picric acid was formed but that the color was due to salts of mononitrophenols.

In spite of the work of Hazen and of Montanari, most of the standard text-books continued to give the reaction as yielding picric acid, ignoring the fact that from a purely theoretical view point it would be very improbable that were a solution of a phenolsulphonic acid poured over a nitrate, trinitrophenol would result.

It appeared desirable, therefore, to the authors to further investigate the method, believing that a solution of the problem might be effected by microchemical methods. Moreover, in the course of routine work in water analysis, various discrepancies in results had been met with upon which light was needed.

It was soon found that no mononitrophenols could be detected in the nitrate-containing water residues which had been treated with phenolsulphonic acid and that no picric acid seemed to be formed until the amount of nitrate reagent rose to very high values and then only traces.

It appeared more probable that nitro groups are introduced into the sulphonic acid and that the yellow color when alkali is added is due to salts of nitrosulphonic acids. As the investigation proceeded it was seen that it would first be necessary to study the sulphonic acids of phenol, since the literature contained many conflicting statements. A discussion of the literature has not been thought necessary by the authors, but it has been compiled and will be found at the end of the present paper. While the work was in progress Obermiller (46) published the results of his exhaustive investigation of these compounds; however, since our work had proceeded so far it was thought wise to continue and confirm the findings of Obermiller in so far as they touched upon our microchemical methods. Following substantially the same methods as those of this investigator, the pure barium salts of the orthosulphonic acid, the parasulphonic acid, the di-2-4- and the tri-2-4-6-acids were prepared. All attempts to prepare a pure barium salt of the monometa acid failed.

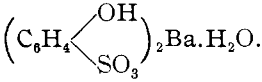
The barium salt of the 2-4-di-acid is the least soluble and separated long before either the ortho or para salts. It crystallizes in beautiful clear, brilliant, colorless, highly refractive prisms and tables, Fig. 1. It has the formula $C_6H_3OH(SO_3)_2Ba.4H_2O$, and gave on analysis the following results:

Found: Ba, 29.81, 30.02; SO_4, 41.75, 41.67; H_2O, 15.55, 15.74.
Calculated: Ba, 29.76 ; SO_4, 41.62 ; H_2O, 15.61.

After the barium salt of the 2-4-diacid has been separated there appears, on further concentration, long, slender prisms with truncated ends of the barium orthosulphonate, if this acid is present. These crystals are clear, colorless, and tend to separate in bundles, sheaves, rosettes or spherulites (Fig. 2). The purified salt gave, on analysis:

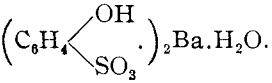
Found: Ba, 27.50, 27.37, 27.41; SO_4, 38.77, 38.83; H_2O, 3.51, 3.54.
Calculated: Ba, 27.39 ; SO_4, 38.30 ; H_2O, 3.59.

It therefore contains one molecule of water of crystallization and has the formula



$$\left(C_6H_4\begin{matrix}\diagup OH\\ \diagdown SO_3\end{matrix}\right)_2Ba.H_2O.$$

The para acid yields a barium salt of such great solubility that it may be prepared quite free from ortho or the di compounds, but has a tendency to form supersaturated solutions refusing to crystallize until solidification takes place, thus rendering its purification somewhat difficult. The pure salt (Fig. 3) forms rosettes of exceedingly slender white needles having a beautiful silky luster, very different in appearance and behavior from the ortho salt with which it is isomeric, having the formula



$$\left(C_6H_4\begin{matrix}\diagup OH\\ \diagdown SO_3\end{matrix}\right)_2Ba.H_2O.$$

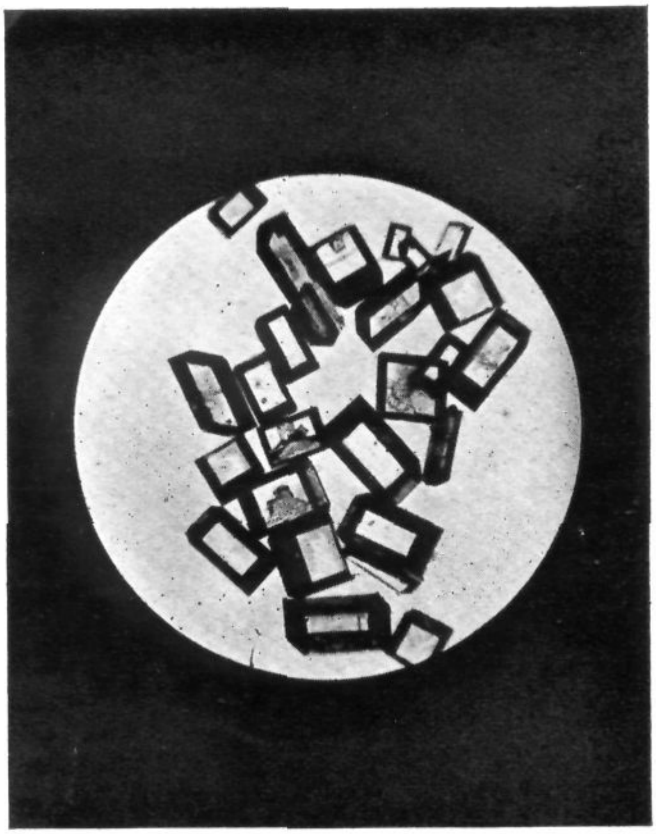


Fig. 1.—Barium salt of 1,2,4-phenolsulphonic acid × 15.

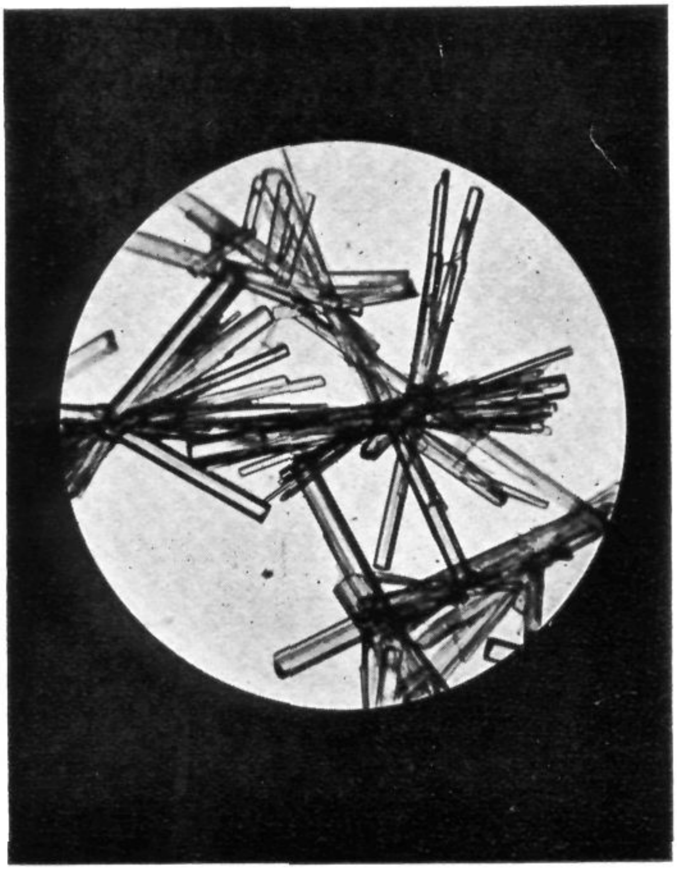


Fig. 2.—Barium salt of orthophenolsulphonic acid × 30.

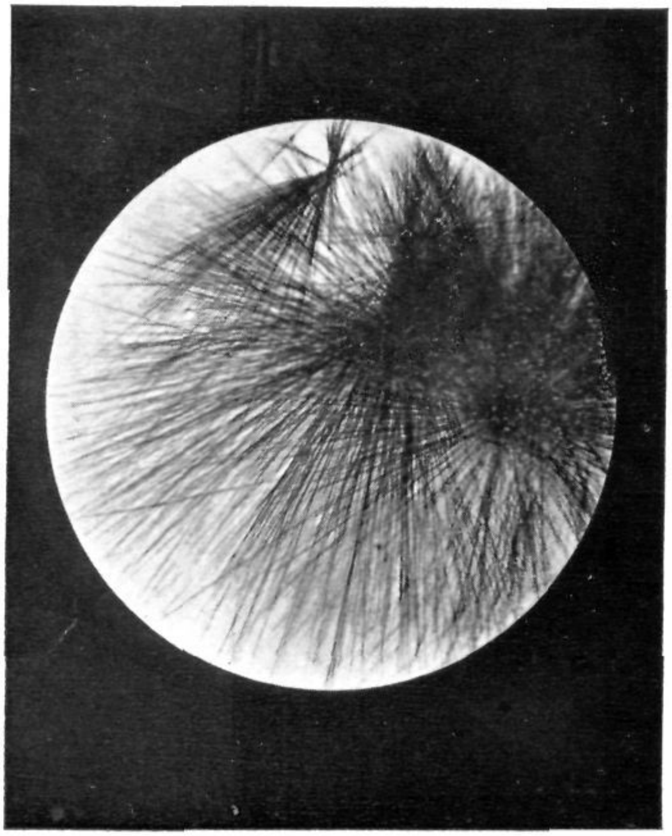


Fig. 3.—Barium salt of paraphenolsulphonic acid × 30

Found: Ba, 27.53, 24.40, 27.44; SO_4, 39.18, 39.91; H_2O, 3.62, 3.60.
Calculated: Ba, 27.39 ; SO_4, 38.30 ; H_2O, 3.59.

The trisulphonic acid of phenol is formed only at high temperatures and under pressure (47, 48). The barium salt prepared according to the method of Sanhofer (47) is very insoluble and is crystallizable in hexagonal plates only with great difficulty. Its great insolubility renders its separation from the other sulphonic acid salts, described above, easy and sharp.

No trisulphonic acid could be detected in the sulphonic acid reagents. This was to be expected since this compound appears to be formed only when fuming sulphuric acid and phenol are heated at high temperatures and even then the authors find much of the 2-4-acid formed.

It will be seen from the accompanying photomicrograph of these three salts that they are very different in appearance and that there is no possibility of confusing one with another. With these data in hand it was possible to proceed with the microchemical analysis of the various sulphonic acid reagents which have been proposed for analytical use, but there is also another method of attack, depending upon the behavior of these sulphonic acids toward nitrates and which will be discussed later.

The barium salts were made by adding barium carbonate to the diluted sulphonic acid, until the acid reaction to congo red just changed. After filtration and concentration portions were removed, concentrated and the crystals separating examined under the microscope. The material was either fractionally crystallized on a microscope slide or on a larger scale in small crystallizing dishes. Both methods gave identical results.

In order that there might be no question as to the relative sensitiveness of the different sulphonic acid reagents which have been described by various investigators, every one which we have been able to find in the literature was now prepared and all have been compared one with another. The most satisfactory in final color and delicacy are those obtained by heating phenol and sulphuric acid on the water-bath for not less than five hours. Microchemical analysis of these by means of their barium salts, showed them to consist of the 1-2-4-diacid with a very little para acid. No ortho acid was present and probably no tri-acid. If the reagent be made from phenol and fuming sulphuric acid, only prismatic crystals similar to those of Fig. 1 are obtained, but no ortho or para acid could be found, from which we conclude that under these conditions only the 1-2-4-diacid is formed.

Ofttimes sulphonic acid reagents prepared for water analysis solidify on standing. It was found, on investigation, that all three of the pure acids prepared readily crystallized at room temperature, permitting no sharp separation or differentiation, and that the solidification of a reagent afforded no clue to its probable composition.

By decomposing the pure barium salt of the ortho, para and di acids with sulphuric acid a sulphonic acid could be obtained which would correspond in the main to the salt from which it was formed. These acids were then used as reagents and poured over dry nitrate residues in the usual manner, diluted and made alkaline with ammonium or sodium hydroxide to ascertain the color reaction and intensity of color. It was found that the ortho acid always gives an intense grass-green solution, dichroic like chlorophyll—reddish by transmitted light, green by reflected light--the color is so intense that an amount of over five parts per million of nitrogen as nitrates yields a solution appearing inky black when viewed in colorimeter tubes.

With the para acid there is no change in the cold, no nitro groups apparently being introduced into the compound. If, however, the para acid be heated in contact with a nitrate and the mixture diluted and treated with an alkali, the same dark green solution results as is obtained with the mono-ortho acid. Prolonged heating of either acid with the nitrate residue yields in each case, in the presence of alkali in excess, a yellow solution with greenish tint.

The green compound and the use of the ortho acid as a reagent will be discussed in a second paper.

The 1-2-4-disulphonic acid used as reagent yields with alkali pure yellow solutions, with practically no trace of green. The reagent is not as delicate, however, as the ortho acid.

The behavior of these three sulphonic acids toward nitrates throws light upon the peculiar results published from time to time by previous workers. Reagents giving a greenish tint contain the ortho acid, while reagents lacking in delicacy contain too much para acid.

The yellow compound formed by the action of alkali upon nitrated 1-2-4-phenolsulphonic acid was found to contain no mononitrophenols, probably no dinitrophenols and only the merest traces of picrates; when the quantity of nitrogen as nitrate to be determined fell within the range usually met with in potable water analyses—*i. e.*, 0 to 35 parts per million—the compound formed is a nitrophenolsulphonic acid, the formula of which, together with that of the green compounds obtained from the ortho acid, the authors will discuss in a future communication. The use of sulphonic acids other than those of phenol will also be discussed.

Summary.

It is possible to analyze, microchemically, mixtures of phenolsulphonic acids by means of their barium salts.

The compositions and properties of the barium salts of the ortho and

1-2-4 acids described by Obermiller has been confirmed and a new barium salt of the para acid made and described.

The standard phenolsulphonic acid used in water analysis consists of the 1-2-4-disulphonic acid with small amounts of the para acid.

The ortho acid poured over nitrates, diluted and made alkaline, yields a dark green solution with no shade of yellow. The para acid is unacted upon in the cold, but behaves like the ortho acid if heated in contact with the nitrate. The di acid yields either hot or cold pure yellow solutions.

Prolonged heating of the mono acids with nitrate residues yields a greenish yellow solution, the mono acids having been partly converted into the di acid by the heat treatment.

The yellow color is due to an alkali salt of a nitrophenolsulphonic acid.

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SOLVENTS FOR USE WITH THE MUNROE CRUCIBLE.

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Although when in using the Munroe crucible a succession of determinations of the same analytical radical in similar substances and by a uniform method of analysis are to be made, the analytical product may be allowed to accumulate in the crucible, yet if there be any variation in the analytical material or process the "residue on ignition" must be removed from the felt between each determination. In some instances a part at least may be shaken or blown out, but the felt can be completely cleansed only by the use of solvents, and this method of procedure is an essential feature of the use of the Munroe crucible in such determinations. The selection of solvents involves several considerations such as the effect of the solvent, either alone or in the presence of air or the solvent product, upon the platinum, and its capacity to easily dissolve the "residue on ignition" and to form with it a solution which is readily and completely removed from the felt. While the solubilities and properties of platinum in platinum ware have been widely studied, and precautions to be taken in its use are to be found in the literature (*vide* Prescott and Johnson, *Qual. Chem. Analysis*, **1901**, p. 95), yet the peculiar properties of platinum in a finely divided state, as it exists in platinum felt, have not been studied further than as to its catalytic action. In